Summary of EPA Review of American Water Document

Introduction. EPA conducted an independent technical review of a document on chemical interaction with pipe materials prepared by American Water. That document provides the assumptions and technical basis for the conclusion made by West Virginia American Water (WVAW) that hydraulic flushing would be an adequate decontamination strategy for removal of crude 4-methylcyclohexane methanol (MCHM - CAS #34885-03-5) from the drinking water distribution system and premise plumbing. The two processes assumed to govern the accumulation of MCHM on or within pipe materials were adsorption and permeation.

Six EPA scientists and engineers reviewed the American Water document. The reviewers primarily focused on whether the conclusions presented in the document were supported by valid assumptions, appropriate hypotheses, and relevant literature. The document's conclusions relate to two main topics explored in the American Water document: MCHM attachment to pipe surfaces and sorption of contaminants into polyethylenes.

Limitations. The American Water document and this review focus on MCHM, which is the primary component of crude MCHM, constituting 68% to 89% of the mixture as described in the document [1]. It does not consider the fate and transport of the other components of crude MCHM, glycol ethers, or the degradation products of these chemicals.

MCHM Attachment to Pipe Surfaces. In the document**,** American Water concluded that MCHM had less potential to adsorb to or accumulate on pipe surfaces than chlordane or *p*-dichlorobenzene since MCHM has a lower log P (or log K_{ow}) and that flushing would effectively remove MCHM from the distribution system and home plumbing. This conclusion was based on American Water Works Association Research Foundation (now WaterRF) study #2981 which presented data on adsorption of chlordane and *p*-dichlorobenzene to a number of pipe materials. All EPA reviewers expressed concerns about the conclusion that log P values and data from study #2981 are sufficient to predict the tendency of another chemical to adsorb. Specific concerns include:

The ability to use the data in study #2981 to support this conclusion is limited by the design of study. For instance, the study design implicitly assumed that the contaminant mass that had adsorbed to a pipe surface but not desorbed during the methanol rinse was negligible. This is an important limitation of the study design as not all adsorption interactions are reversible using a short methanol rinse.

Contrary to the conclusions in the document prepared by America Water, the results from the WaterRF study for chlordane and *p*-dichlorobenzene (for which log P values are known) suggest that these compounds do adsorb to PVC, a plastic piping material. Further examination of the data from the WaterRF study shows that sorption cannot be predicted by log P alone; indeed some inorganic contaminants, which by definition do not possess log P values, appear to undergo sorption to various pipe surfaces. This suggests that physical, chemical, biological, and/or system specific processes not represented by log P can impact the fate and transport of MCHM in a drinking water distribution system. Additional evidence that processes not represented by log P are important for predicting adhesion is found in two EPA reports [2, 3] dating back to 2008, which present results of bench and pilot scale experiments designed to test the effectiveness of contaminant persistence on water pipes and removal using flushing. One of those studies [3] showed that sodium fluoroacetate (SFA) persisted on cement mortar and polycarbonate after exposure to water velocities of 1.0, 1.6 and 1.9 ft/sec. SFA has a reported log P lower (more hydrophilic) than MCMH, *p*-dichlorobenzene, and chlordane. Because SFA is ionized in drinking water, ionic and/or electrostatic interactions with the pipe surface likely influenced its persistence. This is experimental indication that log P alone is not a predictor of persistence.

Even if the conclusion that log P was an adequate predictor of adsorption, it would be contingent on the accuracy of the log P value. No experimental values of the log P for MCHM are currently available, so estimation methods are used. Several estimation methods for log P are readily available, rapid, and user friendly. The document relies on the lower of two estimates (Log P = 1.5). Other estimates, as available from the current version of EPA's EPI Suite™, are significantly different (Log P = 2.55). Because it is a log value, the physical phenomena related to adherence underlying the log P value could be **10 times stronger** if some other estimate was used. Thus, it is unclear what effect the selection of log P = 1.5 had on conclusions and decisions based on log P.

The America Water document also asserts that flushing would be sufficient to remove contaminated bulk water from the distribution system and premise plumbing; however, the document does not discuss American Water's system hydraulics, the process which governs the removal of contaminant in the bulk water during hydraulic flushing. Consideration of system hydraulics is important whether or not there was appreciable accumulation of MCHM on pipe materials. If the assumption about MCHM accumulation were true, and there was no appreciable accumulation of MCHM on pipe materials, then a properly designed flushing program could effectively remove the contaminant from the system, but this cannot be assessed without a detailed review of American Water's flushing plan.

Of particular concern to the reviewers is the potential for residual contaminated water to remain in distribution system storage tanks. These tanks are typically modeled as non-ideal continuously stirred-tank reactors (CSTRs). In an ideal CSTR, approximately 90% of the original solution is replaced after turnover of three tank volumes. Thus, if the initial concentration of MCHM in a tank were 1.0 ppm, three tank turnovers would reduce the concentration to approximately 0.1 ppm. The concentration will continue to decrease with additional tank turnovers, but low concentrations of residual contaminant could persist for some time before a sufficient number of turnovers occurred. Furthermore, in a non-ideal CSTR, there can be stratification or dead zones that do not mix efficiently and can result in much longer retention of contaminated water. Large reservoirs of water in household plumbing systems, such as hot water heaters, could also behave as non-ideal CSTRs. Complete draining of contaminated water, and refilling with clean water, may be an effective flushing strategy for large reservoirs (such as distribution system tanks, commercial building tanks and standpipes, etc.) that behave as non-ideal CSTRs. In summary, any hypothesis about the effectiveness of flushing must be proven in the context of the individual system's hydraulics.

Sorption of Contaminants into Polyethylenes. American Water concluded that there was no reason to believe that MCHM would diffuse in polyethylene piping since it was only in the water at concentrations in the ppm range for a few days before flushing. Reviewers expressed concerns about this conclusion for a variety of technical reasons, including:

While there is uncertainty regarding the extent and significance of MCHM permeation into plastic pipes, the available body of knowledge would suggest that permeation of MCHM into plastic pipes exposed to aqueous solutions of MCHM cannot be ruled out. Numerous papers have documented contamination of water in distribution system pipes and service lines due to permeation of organic contaminants through plastic pipes. In one study, seven permeation incidents were documented that involved permeation of gasoline or paint thinner in contaminated soil through the wall of polyethylene (PE) or polybutylene (PB) pipes [4]. Another case study documented the permeation of semi-volatile constituents of gasoline through PB pipe [5]. Controlled laboratory studies evaluated permeation of BTEX compounds (benzene, toluene, ethylbenzene, and xylene) through PE pipes and measured the diffusion coefficients [6]. In another controlled laboratory study, the permeation rate of aqueous phase benzene and tricholoroethylene through 1 inch PVC pipe, with a wall thickness of 0.141 inches, was measured, and complete permeation was observed to occur in 60 to 240 days [7]. Similarly, the solubility and permeability coefficients, which describe the transport of chemicals through polymers exposed to liquids, have been measured for the transport of organic compounds through PE in food storage applications [8]. Key physical properties that contribute to these coefficients are molecular weight, molar volume, and vapor pressure. The values of these physical properties for MCMH fall within the range of those for reported compounds, so it is reasonable to assume that MCMH may permeate a variety of plastic materials. A precise estimate of MCMH solubility and permeability coefficients would require detailed study.

When evaluating the potential for contaminant permeation into polymeric materials used in the construction of water distribution and premise plumbing systems, consideration should be given to the wide range of locations where these materials are used, including: supply pipes, fixtures, gaskets, seals, drain lines, etc. The permeation of contaminants is expected to vary with the specific polymer used [7].

Summary. There is little information available to predict the fate and transport of MCHM in drinking water distribution or premise plumbing systems. However, based on information available in the peer reviewed literature, it is possible that MCHM did accumulate on or within pipe materials through adsorption or permeation. In our review of the document, we concluded that some accumulation of MCHM on or within pipe materials was possible; however, there is insufficient information to estimate the total mass of MCHM that accumulated. What is known from recent results from sampling and laboratory analysis is that most sites had concentrations below the 0.01 ppm detection limit and no sites had concentrations above 1.0 ppm [9], the target concentration for MCHM established by the Centers for Disease Control and Prevention [10].

Under the emergency conditions of a distribution system contamination incident, EPA recommends timely and aggressive response actions to protect public health [11]. These actions can include issuance of public notification with instructions to not use drinking water, which minimizes the potential for public exposure to the contaminant. Another response action is flushing contaminated water from the system. Timely flushing will reduce the time that a contaminant is in contact with distribution system and plumbing pipe materials, which in turn minimizes the accumulation of the contaminant on pipe surfaces.

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